

Enhanced degradation of atrazine under field conditions correlates with a loss of weed control in the glasshouse

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Abstract: Enhanced degradation of atrazine has been reported in the literature, indicating the potential for reduced residual weed control with this herbicide. Experiments were conducted to determine the field dissipation of atrazine in three cropping systems: continuous *Zea mays* L. (CC) receiving atrazine applications each year, *Gossypium hirsutum* L.–*Z. mays* rotation (CCR) receiving applications of atrazine once every 2 years and a no atrazine history soil (NAH). Subsequent laboratory and greenhouse experiments were conducted with soil collected from these cropping systems to determine atrazine degradation, mineralization and residual weed control. Field dissipation of atrazine followed first-order kinetics, and calculated half-life values for atrazine combined over 2003 and 2005 increased in the order of CC (9 d) = CCR (10 d) < NAH (17 d). Greenhouse studies confirmed that the persistence of atrazine was approximately twofold greater in NAH soil than in CC or CCR soil. Biometer flask mineralization studies suggested that enhanced degradation of atrazine was due to rapid catabolism of the *s*-triazine ring. Glasshouse efficacy studies revealed a loss of residual weed control in CC and CCR soil compared with NAH soil. These data indicate that, under typical Mississippi Delta field conditions and agronomic practices, the persistence of atrazine may be reduced by at least 50% if the herbicide is applied more than once every 24 months. Glasshouse studies suggest that under these conditions a loss of residual weed control is possible.

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1 INTRODUCTION

Atrazine [6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5-triazine-2,4-diamine] is a herbicide applied to soil for control of many broadleaf and certain grass weeds in *Zea mays* L. (corn), *Sorghum bicolor* (L.) Moench (sorghum) and *Saccharum officinarum* L. (sugarcane). Historically, atrazine was considered to be slowly biodegradable in soil owing to the halogen and *N*-alkyl substituents, which impede microbial metabolism of the *s*-triazine ring.¹ However, in the mid-1990s, independent laboratories isolated bacteria able to mineralize ring-labeled ¹⁴C-atrazine.^{2,3} Today, genes that code for catabolic mineralization of atrazine have been fully sequenced and characterized, and homologues of these genes have been detected in atrazine-degrading bacteria isolated from geographically distinct regions from around the world.^{4–7} Coinciding with the isolation and identification of bacteria with the ability to mineralize ring-labeled-atrazine, enhanced degradation of atrazine in agricultural soils was reported in several countries, e.g. Argentina, Belgium, Canada, France and the United States.^{8–15} The development

of enhanced atrazine degradation has been positively correlated with atrazine exposure history and soil pH.^{8–10,12–15} This indicates that the application of atrazine to some agricultural soils selects for a microbial population with the ability rapidly to degrade the herbicide. Coincidentally, residual weed control should be reduced in soils that exhibit enhanced degradation of atrazine; however, this has not been confirmed. The objective of this study was to determine the field persistence of atrazine in soils with different atrazine exposure histories, and to relate the persistence of atrazine in these soils to residual weed control.

2 EXPERIMENTAL METHODS

2.1 Field dissipation of atrazine

A six-year field study was conducted from 2000 through 2005 at the USDA Southern Weed Science Research Unit farm, Stoneville, MS (33°26'N). The soil was a Dundee silt loam (fine-silty, mixed, thermic Aeric Ochraqualf) with pH 6.7, 1.1% organic matter, a CEC of 15 cmol kg^{–1} and soil textural fractions of 26% sand, 55% silt and 19% clay. Before initiation of

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the study, the experimental area was under glyphosate-resistant *Glycine max* L. (soybean) production and had no known atrazine exposure for at least 20 years. Field preparation consisted of disking, subsoiling, disking and bedding in the fall of 1999. The old seedbeds (0.1 m wide) were raised (rebedded) in the fall of each year beginning in 2000 after harvest. Beds were smoothed as needed to plant crops in the spring.

The field experiment was conducted as a randomized complete block with four replications. Experimental units consisted of eight rows spaced 0.1 m apart and 45.7 m long. Soils of three cropping systems were evaluated for enhanced degradation of atrazine: (1) a continuous conventional corn cropping system that received applications of atrazine each year (CC); (2) a conventional *Gossypium hirsutum* L. (cotton)–corn rotation (1:1) where plots received applications of atrazine once every 2 years starting in 2001 (CCR); and (3) a no atrazine history soil (NAH1) from a glyphosate-resistant (GR) corn–cotton rotation system that did not receive an application of atrazine until the sixth year of the study when plots were planted in a conventional corn variety.

To control existing weeds, the experimental area was treated with paraquat (1.1 kg AI ha⁻¹) 1–4 d before planting the crop. Conventional and GR cultivars of cotton and corn were planted in 102 cm wide rows. Cotton and corn varieties, planting dates, herbicides and application timings and harvest dates are presented in Tables 1, 2 and 3. A glyphosate-based program in GR cultivars and a non-glyphosate-based program in non-GR (conventional) cultivars were used for weed control. Herbicide treatments were applied with a tractor-mounted sprayer with TeeJet 8004 standard flat spray tips (Spraying Systems Co., Wheaton, IL) delivering 187 L ha⁻¹ water at 179 kPa. Fertilizer application and insect control programs were standard for cotton and corn production.^{16,17} Crops were furrow irrigated as needed.

Field dissipation of atrazine in CC and CCR soil was monitored in 2003 and 2005. Dissipation of atrazine in NAH1 soil was monitored only in 2005 when a conventional variety was planted and atrazine was included in the weed control program. From 0 to 32 d after the initial application of atrazine, composite soil samples were collected from three locations in each plot to a depth of 5.0 cm. At each location, two samples were collected from in the plant row and two samples were collected from the furrow between the beds. Composite samples were thoroughly mixed, and a subsample (50 g) was removed for herbicide analysis. Soil samples were stored at –5 °C until initiating extractions, typically within 4 d. Field dissipation of atrazine was fitted to the equation

$$C = C_0 e^{-kt} \quad (1)$$

where C_0 is the concentration of atrazine in soil at time zero (mg kg⁻¹), k is the first-order rate constant (d⁻¹)

and t is time (d). Half-life ($T_{1/2}$) values for atrazine in soil were calculated from the equation

$$T_{1/2} = \ln 2/k \quad (2)$$

2.2 Laboratory and greenhouse studies

2.2.1 Soil collection for laboratory and greenhouse studies

In October 2005, after harvest, soil was collected from CC and CCR plots as previously described in Section 2.1. Laboratory mineralization experiments indicated the development of enhanced atrazine degradation in NAH1 (Zablotowicz RM, private communication, 2005), likely due to redistribution of soil from atrazine-adapted soil during bed formation in the spring. Thus, soil was collected from GR continuous cotton plots located adjacent to the original study site (NAH2). The soil type for NAH2 was the same as for NAH1, Dundee silt loam, and the chemical/physical properties were similar among locations. The NAH2 plots had been in cotton since 1997 and had no known atrazine application history for at least 20 years at the time of sampling.

2.2.2 Mineralization

Mineralization of ¹⁴C-ring-labeled atrazine was evaluated in biometer flasks. The experiment was conducted as a randomized complete block with four replications. Soil (25 g dry weight equivalent) from CC, CCR and NAH2 plots was fortified with a solution of technical-grade atrazine (99% purity; Chemserv, Lancaster, PA) and ¹⁴C-atrazine (115 µCi mmol⁻¹ specific activity, 94% radiological purity; Sigma Chemical Company, St Louis, MO) in deionized water. The initial herbicide concentration was 4 µg g⁻¹ and the initial radioactivity was 190 Bq g⁻¹. Biometers were incubated in the dark at 25 °C. Evolved ¹⁴C-carbon dioxide was trapped in sodium hydroxide and quantified by liquid scintillation spectroscopy (LSS) using Hionic-Fluor (Perkin Elmer, Shelton, CT). To avoid saturation by carbon dioxide, sodium hydroxide was replaced after each sampling. Soil was destructively sampled at 56 d. Air-dried soil was manually crushed into uniform particle size, and duplicate samples (0.30 g) were weighed onto Whatman 1 qualitative filter paper (Whatman Inc., Florham Park, NJ). Samples were combusted in a Packard model 306 oxidizer (Packard Instruments, Chicago, IL), and evolved ¹⁴C-carbon dioxide was trapped in scintillation vials containing Carbo-Sorb and Permafluor (1 + 1 by volume, 20 mL; Packard Elmer, Meridian, CT). Radioactivity was determined by LSS. The amount of ¹⁴C-carbon dioxide recovered from the combusted samples was added to the cumulative ¹⁴C-carbon dioxide evolved to determine the mass balance of ¹⁴C. Cumulative mineralization of ¹⁴C-carbon dioxide was fitted to the equation

$$Y = A_0 (1 - e^{-kt}) \quad (3)$$

where A_0 is the maximum amount of ¹⁴C-carbon dioxide evolved (% of initial added), k is the first-order

Table 1. Production practices used in the continuous *Zea mays* L. (corn) system at Stoneville, 2000–2005^{a,b}

Production practice	2000	2001	2002	2003	2004	2005
Variety	Pioneer 3223	Pioneer 3223	Pioneer 3223	Pioneer 3223	Pioneer 3223	Pioneer 3223
Planting date	7 April	22 March	5 April	31 March	24 March	1 April
PRE (at planting)	Atrazine + metolachlor	Atrazine + metolachlor	Atrazine + metolachlor	Atrazine + metolachlor	Atrazine + metolachlor	Atrazine + metolachlor
EPOST (3–4 WAP)	None	None	None	None	None	None
PD (5–9 WAP)	None	Atrazine + metolachlor	None	Atrazine + metolachlor + carfentrazone	Atrazine + metolachlor + bentazon	Atrazine + metolachlor + bentazon
Harvest date	14 August	16 August	28 August	18 August	10 August	18 August

^a Abbreviations: EPOST, early post-emergence; PD, post-emergence directed to base of the crop plant; PRE, pre-emergence; WAP, weeks after planting cotton.

^b Rates of herbicides, g AI ha⁻¹: atrazine 1820 + metolachlor 1410 as PRE; atrazine 950 + metolachlor 740 + carfentrazone 9 or bentazon 840 as PD.

Table 2. Production practices used in *Zea mays* L. (corn)–*Gossypium hirsutum* L. (cotton) rotation (1:1) system at Stoneville, 2000–2005^{a,b}

Production practice	2000	2001	2002	2003	2004	2005
Crop	Cotton	Corn	Cotton	Corn	Cotton	Corn
Variety	Stoneville 474	Pioneer 3223	Stoneville 474	Pioneer 3223	Sure-grow 747	Pioneer 3223
Planting date	11 May	22 March	1 May	31 March	22 April	1 April
PRE (at planting)	Fluometuron + metolachlor	Atrazine + metolachlor	Fluometuron + pendimethalin	Atrazine + metolachlor	Fluometuron + metolachlor	Atrazine + metolachlor
EPOST (3–4 WAP)	Pyriothibac	None	Pyriothibac	None	Pyriothibac	None
PD (5–9 WAP)	Sethoxydim	Atrazine + metolachlor	Fluometuron + MSMA	Atrazine + metolachlor + carfentrazone	Fluometuron + MSMA	Atrazine + metolachlor + bentazon
Harvest date	22 September	16 August	23 September	18 August	23 September	18 August

^a Abbreviations: EPOST, early post-emergence; PD, post-emergence directed to base of the crop plant; PRE, pre-emergence; WAP, weeks after planting cotton.

^b Rates of herbicides, g AI ha⁻¹: fluometuron 1120–1680 + metolachlor 1120–1680 or pendimethalin 1120 in cotton and atrazine 1820 + metolachlor 1410 in corn as PRE; atrazine 950 + metolachlor 740 + carfentrazone 9 or bentazon 840 in corn as PD; pyriothibac 105 in cotton as EPOST; sethoxydim 280 +, fluometuron 896 + MSMA 2240 in cotton as PD.

Table 3. Production practices used in no atrazine history glyphosate-resistant *Zea mays* L. (corn)–*Gossypium hirsutum* L. (cotton) rotation (1:1) system at Stoneville, 2000–2005^{a,b}

Production practice	2000	2001	2002	2003	2004	2005
Crop	Corn	Cotton	Corn	Cotton	Corn	Corn
Planting date	7 April	18 April	5 April	22 April	24 March	1 April
Variety	AG RX 738RR	DP 436RR	AG RX 738RR	DP 436RR	DKC 69-71RR2/YG CB	Pioneer 3223
PRE (at planting)	None	Fluometuron + pendimethalin	None	Fluometuron + pendimethalin	None	Atrazine + metolachlor
EPOST (3–4 WAP)	Glyphosate	Glyphosate	Glyphosate	Glyphosate	Glyphosate	None
PD (5–9 WAP)	None	None	Glyphosate	Glyphosate	Glyphosate	Atrazine + metolachlor + bentazon
Harvest date	14 August	20 September	28 August	19 September	10 August	18 August

^a Abbreviations: EPOST, early post-emergence; PD, post-emergence directed to base of the crop plant; PRE, pre-emergence; WAP, weeks after planting cotton.

^b Rates of herbicides, g AI (AE for glyphosate) ha⁻¹: fluometuron 1120 in cotton and atrazine 1820 + metolachlor 1410 in corn as PRE; atrazine 950 + metolachlor 740 + bentazon 840 in corn as PD; glyphosate 840 in corn and cotton as EPOST and PD.

rate constant (d⁻¹) and t is time (d). The $T_{1/2}$ value for atrazine mineralization was calculated from Eqn (2).

2.2.3 Atrazine dissipation and residual weed control

Soil (approximately 4.6 kg) from the CC, CCR and NAH2 plots was placed in 0.5 by 0.24 m plastic trays to a depth of 0.04 m. The experiment was conducted in the glasshouse as a randomized complete block with four replications. *Sida spinosa* L., *Amaranthus retroflexus* L., *Ipomoea lacunosa* L. and *Brachiaria platyphylla* (Griseb.) Nash were planted in each tray to determine atrazine efficacy. Seeds (30) of each weed species were planted in a separate row, 0.24 m long. After planting, trays were treated with a commercial formulation of atrazine (1.82 kg ha⁻¹) with an indoor spray chamber equipped with an air-pressurized system at 190 L ha⁻¹ and 140 kPa. Non-treated trays (no atrazine) were included as a control. Immediately following herbicide application, trays were placed in the glasshouse at 35/25 °C with a 14:10 h light:dark photoperiod. Trays were watered in the form of a mist as needed. Soil (approximately 25 g) was collected at 0, 4, 8, 12, 18 and 21 d after herbicide application. Soil samples were extracted immediately, and the concentration of atrazine was determined by high-performance liquid chromatography (HPLC). Plants were clipped at the soil surface and fresh weight was recorded at 21 d after atrazine treatment. Dissipation data were fitted to Eqn (1), and $T_{1/2}$ values were calculated with Eqn (2). Relationships between plant fresh weight and $T_{1/2}$ values were fitted to the sigmoidal logistic model:

$$Y = a/[1 + (X/X_0)^b] \quad (4)$$

where a is the difference of the upper and lower response limits (asymptotes), X_0 is the level of the independent variable that results in a 50% reduction (IC₅₀) in the dependent variable and b is the slope of the curve around X_0 .

2.4 Herbicide analysis

2.4.1 Extraction and concentration

Soil (20–50 g) was agitated with methanol + water (8 + 2 by volume, 100 mL) for 24 h and centrifuged for 10 min at 6000 × g , and the supernatant was removed. The extract was concentrated by rotary evaporation, diluted in water (100 mL) and passed through a C₁₈ solid-phase extraction column (Bakerbond; JT Baker, Phillipsburg, NJ) preconditioned with methanol (4 mL) followed by distilled water (4 mL) under negative pressure. Atrazine was eluted with methanol (2 mL). Terbutylazine was included as an internal standard.

2.4.2 Quantification

Atrazine was identified and quantified with a Waters 2695 HPLC separations module (Waters, Milford, MA) with a Waters 996 photodiode array detector (Waters, Milford, MA). The HPLC was fitted with a

2.1 mm diameter by 150 mm length Waters symmetry C₁₈ column (Waters, Milford, MA). All solvents were HPLC grade and consisted of acetonitrile + water (4 + 6 by volume). Mobile phase flowrate was constant (0.3 mL min⁻¹). Recovery of atrazine was 98.4 ± 4%, and the instrument limit of detection was 0.11 µg mL⁻¹ (*n* = 8).

2.5 Statistics

All regression equations were fitted with Sigma Plot 9.0 (Systat Software Inc., Point Richmond, CA). Pseudo-*R*² values were calculated to assess the goodness of fit for the appropriate equation. The *R*² value was obtained by subtracting the ratio of the residual sum of squares to the corrected total sum of squares from 1. The residual sum of squares was attributed to that variation not explained by the fitted line. The *R*² and residual mean squares were used to determine the goodness of fit to the regression model. Half-life values for atrazine and plant fresh weights were subjected to analysis of variance, and treatment means were separated at the 5% level of significance using Fisher's protected least significant difference test.

3 RESULTS AND DISCUSSION

3.1 Noted problems

During the field experiment, cumulative mineralization of atrazine in NAH1 increased from 9% in 2000 to 58% in 2005 (Zablotowicz RM, private communication, 2005). Enhanced degradation of atrazine in NAH1 soil likely resulted from the transport of atrazine-adapted soil from CC and CCR during seedbed preparation in the spring of each year and other production-related equipment traffic. Consequently, NAH1 exhibited intermediate levels of atrazine degradation; thus, relative differences reported for the degradation potential in atrazine history soils, CC and CCR, compared with NAH1, are likely less than what would have occurred if control plots had not been compromised. To address this problem, soil (NAH2) was collected from an adjacent site that had been under continuous cotton production since 1997 and had no history of atrazine use for at least 20 years.

3.2 Field persistence

For both CC and CCR, the 2003 and 2005 data were pooled. For all treatments, dissipation of atrazine was adequately described by Eqn (1), a first-order kinetics model (Fig. 1). The calculated *T*_{1/2} value for atrazine increased in the order of CC (9 d) = CCR (10 d) < NAH1 (17 d). Thus, the dissipation of atrazine was approximately twofold greater in CC and CCR than in NAH1. These data indicate that, under typical Mississippi Delta field conditions and agronomic practices, the persistence of atrazine in the field may be reduced by 50% if the herbicide is applied at least once every 24 months. Moreover,

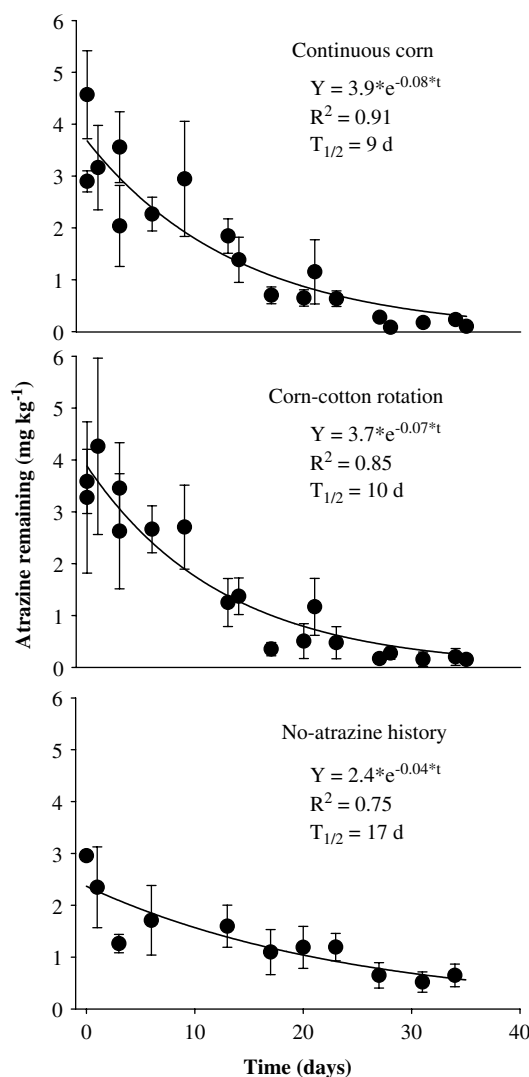


Figure 1. Field dissipation of atrazine combined over 2003 and 2005 for continuous *Zea mays* (corn) plots that have received annual applications of atrazine since 2000, corn-*Gossypium hirsutum* (cotton) rotation (1:1) plots that have received applications of atrazine once every 2 years and plots with no prior exposure to the herbicide atrazine. Symbols represent the mean of four replicates. Error bars indicate one standard deviation and do not appear when smaller than the symbol for the mean. Fitted values, indicated by the smooth line, are the best fit of the first-order kinetics model $Y = A_0 e^{-kt}$, where A_0 is the amount of atrazine in soil at time zero (mg kg⁻¹), k is the first-order rate constant (d⁻¹) and t is time (d). The half-life (*T*_{1/2}) value for atrazine in soil was calculated from the relationship $T_{1/2} = \ln 2/k$.

since the mineralization potential of NAH1 increased sixfold from 2000 to 2005, it is likely that the relative decrease in the persistence of atrazine in CC and CCR compared with NAH1 would have been greater had the control plots not exhibited elevated levels of atrazine degradation. To the authors' knowledge, this is the first report of enhanced degradation of atrazine in a replicated field study. Researchers have reported enhanced degradation of atrazine in non-replicated, large-scale field screening studies.⁸⁻¹⁵ In all cases, persistence of atrazine under field conditions was not evaluated; only laboratory mineralization and/or dissipation studies were conducted. When enhanced degradation of atrazine was noted, the half-life of

atrazine in soil was <10 d, and mineralization of ^{14}C -ring-labeled atrazine exceeded 60% of the initially added radioactivity after 55 d of incubation.^{8,9,12–15} In contrast, the typical half-life for atrazine in non-adapted soil is 60 d.¹⁸ Enhanced degradation was observed only in soil cultivated to corn and having received applications of atrazine.^{8–14} Although enhanced degradation has been reported for soil after a single exposure to atrazine, the norm is an exposure history of 2 years or more.^{9,10,12–15,19} It is important to note that not all soils with an atrazine exposure history exhibit enhanced degradation of the herbicide. The adaptation of the microflora responsible for rapid mineralization of the *s*-triazine ring is typically observed only in neutral or high-pH soils.^{10,12,13} Development of enhanced atrazine degradation may be limited to fields cultivated to crops where atrazine is a component of the weed control program and where the pH of the soil is approximately 6.0 or greater, as was the case in the present study. Once microbial adaptation occurs in such fields, it is unclear how long enhanced degradation of atrazine will persist. The authors' research program is currently addressing this issue. In the present study, field dissipation of atrazine was not different between CC and CCR. This indicates that the microbial population responsible for enhanced degradation of atrazine was maintained for at least 24 months after application of the herbicide. Similar observations were noted for a *Triticum aestivum* L. (wheat)–corn rotation (1:1) and a soybean–corn rotation (1:1).^{8,9} Ostrofsky *et al.*¹¹ reported rapid and extensive mineralization of ^{14}C -atrazine in soil collected from a field cultivated to continuous corn and having received annual applications of atrazine, 80% of the initial radioactivity being evolved as ^{14}C -carbon dioxide after 30 d of incubation. In contrast, the mineralization of atrazine in an adjacent field cultivated to a corn–soybean–wheat rotation (1:1:1) was <30% after 30 d of incubation. The implication is that enhanced degradation of atrazine may be controlled if the compound is applied to soil on a 36 month rotation. This may be a critical management practice if enhanced degradation of atrazine results in a loss of residual weed control.

3.3 Laboratory and greenhouse experiments

3.3.1 Dissipation of atrazine in the glasshouse

Similar to the field study, dissipation of atrazine in the glasshouse was adequately described by Eqn (1) (Fig. 2). The calculated $T_{1/2}$ for atrazine increased in the order of CC (2.5 d) = CCR (2.7 d) < NAH2 (5.0 d). Although the rate of atrazine dissipation was greater for all treatments in the glasshouse compared with the field, the trends were identical; dissipation of atrazine in CC and CCR was twofold greater than the dissipation in NAH2. Higher rates of atrazine dissipation in the glasshouse were attributed to warmer temperatures and optimal soil moisture. Thus, there is a need to evaluate the effect of environmental conditions on the dissipation of atrazine in soil that

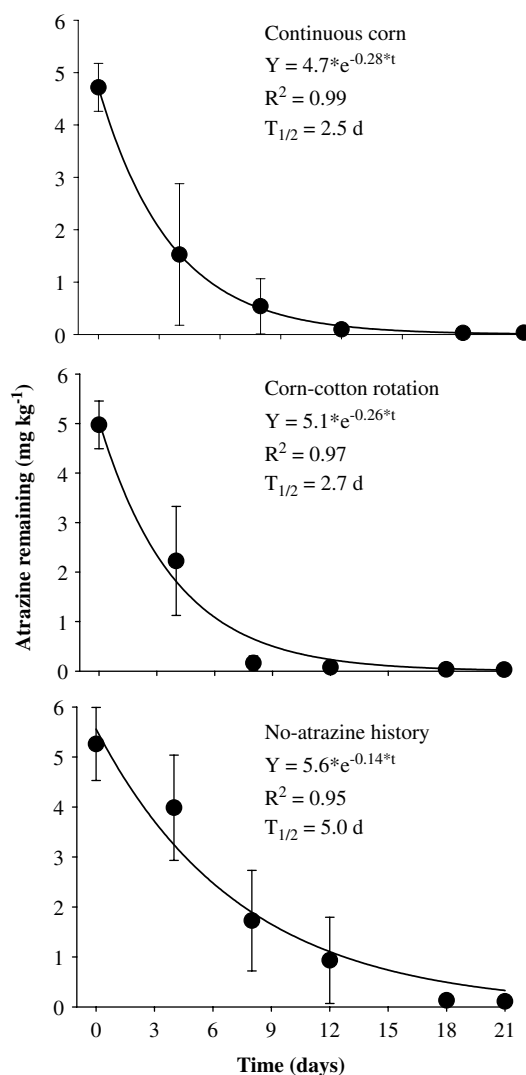


Figure 2. Glasshouse dissipation of atrazine in soils collected in October 2005 after harvest from continuous *Zea mays* (corn) plots that have received annual applications of atrazine since 2000, corn–*Gossypium hirsutum* (cotton) rotation (1:1) plots that have received applications of atrazine every other year and plots with no prior exposure to atrazine. Symbols represent the mean of four replicates. Error bars indicate one standard deviation and do not appear when smaller than the symbol for the mean. Fitted values, indicated by the smooth line, are the best fit of the first-order kinetics model $Y = A_0 e^{-kt}$, where A_0 is the amount of atrazine in soil at time zero (mg kg^{-1}), k is the first-order rate constant (d^{-1}) and t is time (d). The half-life ($T_{1/2}$) value for atrazine in soil was calculated from the relationship $T_{1/2} = \ln 2/k$.

exhibits enhanced degradation. In addition, although NAH2 had never received a known application of atrazine prior to initiating the study, dissipation of atrazine was rapid. As was the case for NAH1, this was likely due to bed reformation in the spring and other agronomic traffic.

3.3.2 Mineralization

For all treatments, the mineralization of ^{14}C -ring-labeled atrazine was adequately described by Eqn (2). Cumulative mineralization and ^{14}C -carbon dioxide evolution during the 56 d incubation was similar among all treatments, approximately 70% (Fig. 3).

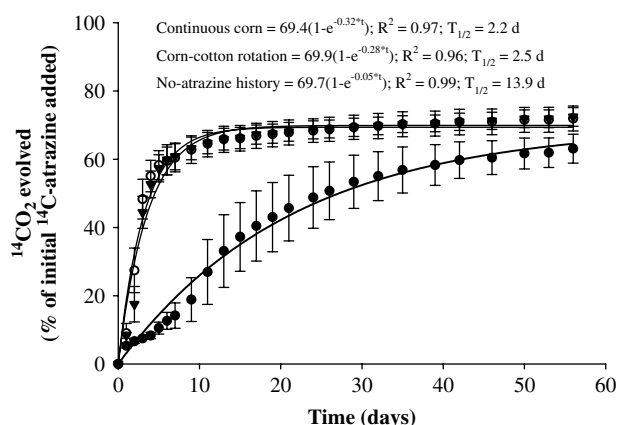


Figure 3. Cumulative mineralization of ^{14}C -ring-labeled atrazine from soil collected in October 2005 after harvest: (O) continuous *Zea mays* (corn) plots that have received annual applications of atrazine, (▼) corn–*Gossypium hirsutum* (cotton) rotation (1:1) plots that have received applications of atrazine once every 2 years and (●) plots with no prior exposure to atrazine. Symbols represent the mean of four replicates. Error bars indicate one standard deviation and do not appear when smaller than the symbol for the mean. Fitted values, indicated by the smooth line, are the best fit of the first-order kinetics model $Y = A_0(1 - e^{-kt})$, where A_0 is the maximum amount of $^{14}\text{CO}_2$ evolved (% of initial radioactivity added), k is the first-order rate constant (d^{-1}) and t is time (d). The half-life ($T_{1/2}$) value for atrazine in soil was calculated from the relationship $T_{1/2} = \ln 2/k$.

However, the rate of mineralization was fivefold greater in the atrazine history soils, CC and CCR, than in NAH2. Others have reported that cumulative mineralization of ^{14}C -ring-labeled atrazine in soils that exhibit enhanced degradation of atrazine exceeded 60% of the initially added radioactivity after 55 d of incubation.^{8,9,13,14} The present mineralization data indicate that enhanced degradation of atrazine in the field and glasshouse is likely due to the development of a microbial population with the ability rapidly to mineralize the *s*-triazine ring. Seven bacterial strains were isolated from the atrazine-adapted soils that were able rapidly to mineralize ring-labeled atrazine as a sole nitrogen source. Currently, the authors are screening these isolates for the *atz* genes. A detailed description of these isolates and their metabolic capabilities will be described in a forthcoming manuscript.

3.3.3 Residual weed control in the glasshouse

Attempts were made to relate the persistence of atrazine to weed control efficacy under field conditions. At the time of corn planting in 2005, *Chenopodium album* L., *Sesbania exaltata* (Raf.) Cory, *I. lacunosa* and *S. spinosa* were seeded with corn. Weed emergence was recorded periodically up to 3 May 2005. However, for both the atrazine-treated and non-atrazine-treated plots, weed densities were too low to justify reporting. Therefore, atrazine dissipation and efficacy on weeds was monitored in the glasshouse using soil collected after the harvest in 2005.

Weed species evaluated in the greenhouse efficacy experiment were selected on the basis of their reported sensitivity to atrazine: *B. platyphylla* \ll *I. lacunosa* = *S. spinosa* < *A. retroflexus*.¹⁶ The fresh weights of

Table 4. Fresh weight of *Brachiaria platyphylla* (BP), *Sida spinosa* (SS), *Amaranthus retroflexus* (AR) and *Ipomoea lacunosa* (IL) in continuous *Zea mays* (CC), *Zea mays*–*Gossypium hirsutum* rotation (1:1) and a no atrazine history soil (NAH2). Soils were treated with atrazine at 1.82 kg ha^{-1} , and foliage fresh weight was determined 21 d after planting. Non-treated NAH2 soil was used as a control

Soil	Fresh weight				Fresh weight			
	BP	SS	AR	IL	BP	SS	AR	IL
	(mg/tray)				(mg/plant)			
CC	1031	344	56	3401	64	19	8	293
CCR	1001	491	55	2427	58	21	9	257
NAH2	226	19	0	198	28	10	0	74
Control ^a	306	333	257	4984	38	24	35	406
LSD _(0.05)	NS ^b	201	115	1789	NS ^b	7	21	130

^a Non-atrazine-treated NAH2 soil was used as a control.

^b NS, not significant.

S. spinosa and *I. lacunosa* were greater in CC and CCR than in NAH2 (Table 4). The fresh weight of *A. retroflexus* was greatly reduced in these soils compared with the no-atrazine control. *Amaranthus retroflexus* is more sensitive to atrazine than either *S. spinosa* or *I. lacunosa*; as a result, atrazine remaining in the soil at the time of *A. retroflexus* emergence was sufficient to cause injury. These data indicate that the efficacy of atrazine was reduced in the atrazine history soils, CC and CCR, compared with NAH2. Moreover, fresh weight was negatively correlated with atrazine $T_{1/2}$ values, indicating that reduced efficacy of atrazine is associated with enhanced degradation (Fig. 4). Lack of a significant loss of efficacy on *B. platyphylla* may have been due to two reasons. First, atrazine is less active on *B. platyphylla* compared with the other three weed species.¹⁶ Second, *B. platyphylla* took about 5 d longer to emerge than other weed species, and it is likely that less atrazine was available at this time owing to enhanced degradation. Atrazine is a photosystem II inhibitor. Plants exposed to soil applications of atrazine will germinate and emerge, absorb the herbicide from the soil through their roots and translocate the herbicide to the leaves, where photosynthesis is inhibited.²⁰ Therefore, for atrazine to be active, weeds must emerge and absorb the herbicide. Corn is usually planted between 25 February and 10 April in southern Mississippi and between 15 March and 25 April 25 in northern Mississippi.¹⁶ Weeds usually do not germinate and emerge before April owing to cool temperatures. Consequently, applying atrazine to soil in corn earlier than April may reduce its efficacy owing to no or limited emergence of weeds in early planted corn and enhanced degradation of the herbicide in continuous corn or corn rotated with cotton every other year. This raises questions of the efficacy and economic benefits of soil-applied atrazine in early planted corn. Corn producers can potentially eliminate soil applications of atrazine in early planted corn and use atrazine for post-emergence applications, if needed. Such a practice not only minimizes production costs but also

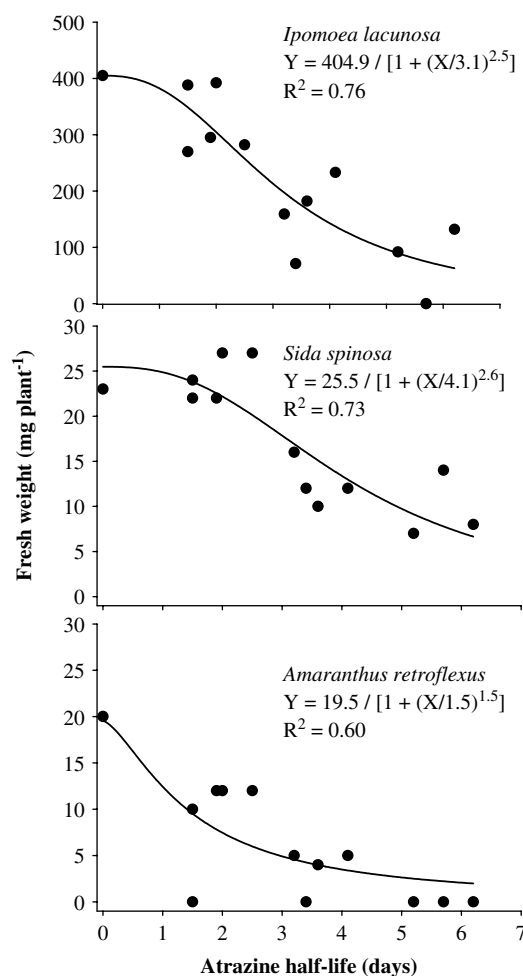


Figure 4. Relationship between the half-life of atrazine in soils collected in October 2005 after harvest and shoot fresh weight of *Ipomoea lacunosa*, *Sida spinosa* and *Amaranthus retroflexus*. Fitted values, indicated by the smooth line, are the best fit of the sigmoidal logistic equation $Y = a/[1 + (X/X_0)^b]$, where a is the difference of the upper and lower response limits (asymptotes), X_0 is the level of the independent variable that results in a 50% reduction (IC_{50}) in the dependent variable and b is the slope of the curve around X_0 .

minimizes the potential for off-site transport of the herbicide.

4 CONCLUSIONS

The dissipation of atrazine under field and glasshouse conditions was approximately twofold greater in atrazine history soil compared with soil with no known prior exposure to the herbicide. Biometer flask data indicated that the mineralization of ^{14}C -ring-labeled atrazine was more rapid in soil with an atrazine exposure history than in soil with no known exposure to the herbicide. Mineralization data suggest that enhanced atrazine degradation is likely due to the development of a microbial population with the ability rapidly to mineralize the *s*-triazine ring. Recently, the authors isolated seven bacterial strains from the atrazine-adapted soils that had the ability rapidly to mineralize ring-labeled atrazine as a sole nitrogen source, and they are currently screening these isolates for the presence of the *atz* genes. These isolates and

their metabolic capabilities will be described in detail in a forthcoming manuscript. Fresh weight of the evaluated weed species in the glasshouse was greater in atrazine history soil than in soil with no prior exposure to the herbicide. Moreover, plant fresh weight was negatively correlated with the persistence of atrazine in these soils. Field persistence data for atrazine coupled with the glasshouse weed efficacy data indicated the potential for loss of residual weed control with atrazine in soils that exhibit enhanced degradation. However, owing to poor weed stand densities, the authors were not able to evaluate the effect of enhanced atrazine degradation on residual weed control with this herbicide under field conditions. Current studies in Elizabeth, Mississippi, are under way to determine if there is a loss of residual weed control in soils that exhibit enhanced atrazine degradation.

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